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(6) COHERENT ANTI-STOKES RAMAN SPECTROSCOPY

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COHERENT ANTI-STOKES RAMAN SPECTROSCOPY

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ABSTRACT

We have carried out the first high resolution cw CARS measurements of H_2, D_2 and CH_4. ~~Our~~ The preliminary experimental results have verified the predicted CARS signal strengths and CARS lineshapes. ~~Our~~ The measurements have shown that ultra-high resolution Raman spectroscopy by the cw CARS method is a very useful spectroscopic tool.

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COHERENT ANTI-STOKES RAMAN SPECTROSCOPY

I. INTRODUCTION

With the publication of "Coherent Anti-Stokes Raman Spectroscopy" by R.F. Begley, A.B. Harvey and R.L. Byer in 1974,[1] CAR spectroscopy emerged as a tool of real interest to chemists and Raman spectroscopists. Subsequent publications[2,3,4,5,6] served to more fully describe the potential of tunable lasers applied to this coherent form of Raman spectroscopy. Thus, CAR spectroscopy, which had been discovered over a decade ago by Maker and Terhune[7] and recently investigated by Levenson[8] and DiMartini[9] is being actively pursued by a number of spectroscopists. The impact of this method of Raman Spectroscopy has now penetrated the commercial suppliers of tunable laser sources who have responded by assisting whenever possible in making equipment available for preliminary investigations.[10,11]

The advantages and disadvantages of CAR spectroscopy have been discussed in the literature.[3] Briefly, CAR spectroscopy offers higher conversion efficiency, greater resolution and significantly better fluorescence suppression than incoherent Raman spectroscopy. These advantages have been demonstrated in recent experiments.[6] However, to date CAR spectroscopy theory and experiment have not been quantitatively compared in detail. The thrust of this program is to carry out detailed theoretical analysis and careful single mode quantitative experiments to verify the CAR spectroscopy method.

II. BRIEF REVIEW OF CARS THEORY

A. Introduction

For reference, the theory of CAR scattering is briefly summarized here. The driving polarization is

$$P(\omega_s) = \epsilon_o \chi^{(3)} (\omega_s, \omega_p, \omega_s, -\omega_p) E_p E_s E_p^*$$

For Raman scattering the input fields are the pump electric field squared, $(E_p E_p^*)$ and quantum noise at the Stokes field E_s. Thus the above polarization describes Raman scattering when used in Maxwell's Equations driven by the polarization P. For CAR spectroscopy

$$\chi^{(3)}(\text{Raman}) = [\chi^{(3)}(\text{CAR})]^*$$

and the quantum noise field E_s is replaced by a coherent field from a tunable laser. CAR spectroscopy is thus a mixing process that proceeds with a conversion efficiency proportional to $|\chi^3(\text{CAR})|^2$. Since all fields are coherent phase is important and the process obeys the energy and momentum conservation rules previously given in CAR spectroscopy work.

The above susceptibility is related to the Raman cross-section on resonance by

$$\chi''_{CAR} = \frac{c^4}{\hbar \omega_p \omega_s^3 \Delta\omega_r} \left(\frac{d\sigma}{d\Omega}\right)$$

where $\Delta\omega_r$ is the Raman linewidth (fwhm) and $(d\sigma/d\Omega)$ is the measured Raman cross-section for a single polarization input and single polarization output.

We have investigated the linewidth of CAR spectroscopy in gases in detail. Since the scattering efficiency varies as

$$\epsilon \propto \omega_{as}^2 |N\chi''_{CAR}|^2 |h_l|^2 P_p^2$$

where N is the density and h is a focusing overlap integral we find that

$$\epsilon \alpha \frac{1}{\Delta\omega_r^2}$$

in the limit where the natural Raman linewidth or pressure broadened linewidth is greater than the Doppler width.

B. Linewidth

To account for Doppler broadening in the theory some care must be taken in the analysis. We proceeded by integrating the coupled equations and solving for the generated anti-Stokes power per molecule. This expression is similar to that given above but includes a $\text{sinc}^2(\Delta k\ell/2)$ phase synchronism factor. We then integrated over each set of molecules belonging to a given velocity group. The $|\chi''_{CAR}|^2$ dependence means that the normal Maxwell-Boltzmann velocity distribution must be squared and re-normalized. The result is a CAR linewidth due to Doppler broadening that varies as

$$\epsilon \alpha \frac{1}{(\Delta\omega_D')^2}$$

where $\Delta\omega_D' = \Delta\omega_D/\sqrt{2}$ and

$$\Delta\omega_D = 2\omega_R \sqrt{\frac{2kT}{Mc^2} \ell n\, 2} \quad .$$

Thus the Doppler width is determined by the Raman frequency and therefore is comparable to infrared Doppler widths. Furthermore, because of the $|\chi''_{CAR}|^2$ dependence the Doppler width is reduced by $1/\sqrt{2}$.

C. CW CARS

In order to accurately compare theory and experiment a single mode experiment must be performed. We therefore calculated the expected cw conversion efficiency for CARS assuming a 1 watt pump source mixing with a cw dye laser beam (single axial mode) at 1 atm pressure. Table I lists the molecules and spectroscopic factors of interest.

TABLE I

RAMAN SPECTROSCOPIC CONSTANTS FOR H_2, N_2 and O_2

Molecule	Raman Vib$_{-1}$ (cm^{-1})	State	ω_e (cm^{-1})	B_e (cm^{-1})	$d\sigma/d\Omega$ (4880) cm^2/sr
H_2	4155.0	$Q_1(1)$	4395.2	60.8	7.9×10^{-31}
N_2	2330.0	$Q_1(6)$	2359.61	2.010	3.3×10^{-31}
O_2	1555.0	$Q_1(9)$	1580.36	1.446	4.3×10^{-31}

The population factors for the states listed in Table I are H_2 : .4833 ; N_2 : .0336 ; O_2 : 0706 which gives a resultant population density of H_2 : 1.194×10^{19} ; N_2 : 2.045×10^{18} ; O_2 : 1.727×10^{18} at STP. For the cw dye experiment Table II lists the frequencies involved in the CAR spectroscopy experiment.

TABLE II

CARS : cw DYE LASER EXPERIMENT

Molecule	λ_p(Å)	ν_p(cm^{-1})	ν_s(cm^{-1})	ν_ω(cm^{-1})	λ_s(Å)	λ_{AS}(Å)
H_2	4880	20491.8	16336.8	24646.8	6121.2	4057.3
N_2	5145	19436.4	17106.4	21766.4	5845.8	4594.2
O_2	5145	19436.4	17881.4	20991.4	5592.4	4763.8

The corrected cross-sections and linewidths are shown in Table III

TABLE III

CROSS-SECTIONS AND LINEWIDTHS

Molecule	$d\sigma/d\Omega$	$\Delta\nu$(cm^{-1})
H_2	7.9×10^{-31}	$\Delta\nu_d \sim .015$
N_2	2.67×10^{-31}	$\Delta\nu_n \sim .165$
O_2	3.48×10^{-31}	$\Delta\nu_n \sim .144$

Assuming a single axial mode dye laser and argon pump laser at 1 watt power level, the conversion efficiency at photon count rate are shown in Table IV.

TABLE IV

CARS SIGNAL LEVELS

Molecule	Conversion Efficiency	Photon Count Rate
H_2	2.2×10^{-10}	4.4×10^{8}
N_2	8.3×10^{-16}	1.4×10^{3}
O_2	1.3×10^{-15}	3.0×10^{3}

Therefore, the cw experiment is easy to perform in H_2 and somewhat more difficult to do in N_2 and O_2. However, the signal to noise ratio should be good under the assumed conditions. The experimental measurements are described in the next section.

CAR spectroscopy, unlike incoherent Raman spectroscopy, carries with the scattering process the phase of the fields involved. The CAR spectroscopy signal involves a sum over all pertinant intermediate levels or

$$\chi^* = \left(\frac{\Delta N}{4\epsilon_o \hbar^3}\right) \frac{1}{[(\omega_{fi} - \omega_2 - \omega_1) - i\Gamma/2]} \left| \sum_k (\text{CARS}) \right|^2$$

where the last term in χ^* is the sum over all intermediate states connecting the initial and final levels. That sum can be explicitly written in the form

$$\left| \sum_k (\text{CARS}) \right|^2 = \left| \sum_k \frac{\langle f|\mu_2^+|k\rangle \langle k|\mu_1|i\rangle}{(\omega_{ki} - \omega_1)} + \frac{\langle f|\mu_1|k\rangle \langle k|\mu_2^+|i\rangle|}{(\omega_{ki} + \omega_2)} \right|^2$$

where $\mu_\alpha = \bar{\mu} \cdot \epsilon_\alpha$ is the dipole operator. If, in carrying out the CARS scattering experiment, the incident frequency ω, is tuned near a resonance ω_{ki} then that resonance becomes the dominant term in the sum over intermediate

states. The expression for the sum can then be written in two parts : one due to the resonance term and the other to the non-resonance terms. Thus,

$$\left|\sum_{k}(\text{CARS})\right|^2 = \left| \frac{\langle f|\mu_2^+|k\rangle\langle k|\mu_1|i\rangle}{(\omega_{ki} - \omega_1 - i\Gamma_{ki}/2)} + \sum_{k} \frac{\langle f|\mu_2^+|k\rangle\langle k|\mu_1|i\rangle}{\omega_{ki} - \omega_1} + \frac{\langle f|\mu_1|k\rangle\langle k|\mu_2^+|\mu\rangle}{\omega_{ki} + \omega_2} \right|^2$$

$$= |\chi_R + \chi_E|^2$$

In the scattering process, the magnitude of the CARS signal depends on the relative sign of χ_R vs χ_E. By tuning successively closer to the resonance, the phase of χ_R can be compared to that of χ_E and from the deduced phase the relative sign of the matrix element derived. Experiments along this line have been performed by Vriens[12,13] in atomic vapors by spontaneous Raman scattering using an argon ion laser source.

III. SUMMARY OF EXPERIMENTAL RESULTS

Using borrowed lasers and detection equipment we have carried out the first high resolution cw CARS spectroscopic measurements. The work was performed during a three month period with most of the results generated during the final week.

Since these preliminary experiments, we have been designing and completing a more sophisticated experimental arrangement for high resolution cw CARS spectroscopy. The apparatus is now being aligned and measurements should begin in a few weeks. A quick comparison of our previous temporary cw CARS experiment with the present set up is useful.

In our earlier experiment we had .6W of argon ion laser power and 20 mW of cw dye laser power. We generated approximately 10^6 photons per second at the exit of the H_2 cell but only detected approximately 10^4 photons per second after the filter and spectrometer system. The detection method used direct photon counting with a cooled photomultiplier tube. In our permanent set up we have up to 4 Watts of argon ion laser power and 100 mW of dye power. The spectrometer-filter system is two orders of magnitude more efficient and the detection system is phase sensitive which allows signal-to-noise improvement of approximately 100. The net result is an overall signal-to-noise improvement of approximately 10^6. Therefore, as impressive as our early results were, we expect to improve on them dramatically with the present system.

In our first experiments we detected and measured CARS signals in H_2, D_2 and CH_4. Our resolution was 30 MHz and signal-to-noise ratio was near 50. Linewidths and pressure broadened lineshapes were measured from the Doppler broadened low pressure through the Dicke narrowing range to the pressure broadened regime at up to 20 atm. The results for H_2 and D_2 were presented at the Amsterdam Quantum Electronics Conference and published in a brief note.[14] The paper is presented as Appendix I of this report. Our methane measurements were discussed in more detail in a short paper[15] and are presented as Appendix II. Finally, collision narrowing results were discussed for H_2 and D_2 leading to values of diffusion coefficiently in a recent paper.[16] The abstract is given in Appendix III.

IV. CONCLUSIONS

We are now completing our cw CARS experimental set up. The system will use a high power Kr ion laser source mixing with a cavity dumped argon ion laser pumped cw dye laser. The Kr ion laser is to operate in a single axial mode with feedback control for maximum stability. We have designed special prism filters to eliminate plasma light at the laser output and to reduce pump light after the gas cell. The spectrometer will use a low scatter holographic grating for optimum spectral filtering. The detection system is a cooled photomultiplier tube and a phase sensitive photon counter with computer compatable output. We plan to interface the data taking and reducing with our PDP11E10 minicomputer. Finally, cavity dumping of the argon ion laser is being planned in order to increase the peak power to 100 W. This results in two orders of magnitude increased signal power for application to CARS spectral measurements where the linewidth is broadened such as gases at high pressure, in flames or liquids.

We plan investigations of linewidth lineshape and absolute Raman frequency measurements of H_2 , D_2 and HD. Following these measurements we plan to investigate methane in detail to resolve hyperfine structure. Using H_2 we also plan to make a detailed study of CARS for full quantitative verification of the theory.

There is no doubt, based on our previous measurements, that cw CARS will be an important high resolution tool in molecular spectroscopy.

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APPENDIX I

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CW HIGH RESOLUTION CAR SPECTROSCOPY OF H_2 , D_2 , and CH_4

by

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May 1976

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CW HIGH RESOLUTION CAR SPECTROSCOPY OF H_2, D_2, AND CH_4

by

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We have fully resolved the Raman Q branch lines of H_2, D_2 and CH_4 from 0.3 to 15 atm, using cw four-wave Raman mixing. Figure 1 shows the linewidth vs pressure of the Q(1) 4155.21 cm^{-1} line of H_2 and the Q(2) 2987.18 cm^{-1} line of D_2 at room temperature from the pressure broadened regime, through the collision narrowed minimum to the CARS Doppler broadened limit at low pressures. The resolution, limited by the relative stability of the single axial mode dye laser and argon-ion laser was 30 MHz. The shape and minimum of the linewidth vs pressure curves agree with theoretical predictions by Galatry[1] and by Rautian and Sobel'man[2] and with earlier experimental results at high pressure taken by Javan,[3] using a stimulated Raman gain measurement technique and by De Martini[4] using pulsed Raman mixing.

The resolution of cw CAR spectroscopy at low pressures is limited by the CARS Doppler linewidth, which is $1/\sqrt{2}$ of the usual Raman Doppler linewidth. For H_2 and D_2 we calculate a full width at half maximum of 770 MHz and 391 MHz, respectively, and for pure rotational Raman, the linewidth reduces to tens of megahertz.

In our experiment we mixed a single axial mode Spectra Physics cw dye laser against a single axial mode argon-ion laser, operating at either 0.4880 μm or 0.5145 μm. For 10 mW of input dye laser power and 640 mW of argon-ion laser power focussed into the gas sample, with an optical system collection efficiency at the anti-Stokes wavelength of approximately 1.36%

for H_2 and 0.53% for D_2 and CH_4, the estimated photon count rates are 2×10^6 Hz for H_2 at 5 atm, 8.5×10^4 Hz for D_2 at 3 atm, and 1.4×10^5 Hz for CH_4 at 6 atm. Our observed count rates were within two orders of magnitude of the above estimates. Although cw CARS mixing has been observed previously,[5] this is the first experiment that demonstrates its potential for ultra-high resolution gas phase Raman spectroscopy.

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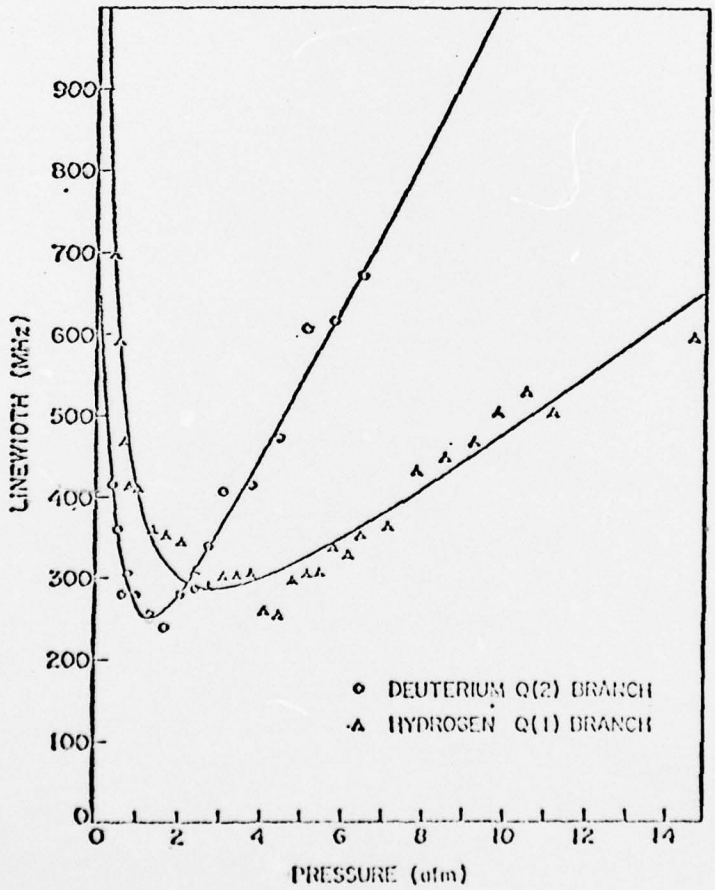

Figure 1

cw high resolution CAR spectroscopy of the $Q(\nu_1)$ Raman line of methane

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Coherent anti-Stokes Raman spectroscopy offers the possibility of obtaining high resolution Raman spectra of gases limited only by the resolution of laser sources. Previously CAR spectroscopy has been carried out using high peak power laser sources to maintain high conversion efficiency but at a loss in resolution.[1,2,3] For example, pulsed dye laser sources offer a resolution of 0.1 cm^{-1} (3000 MHz) compared to cw dye laser linewidths of less than 0.001 cm^{-1} (30 MHz). Recently cw CARS has been used to detect methane[4] and nitrogen[5,6] and to measure collision narrowed linewidths in H_2 and D_2.[7]

Figure 1 shows a schematic of the experiment. We used a single axial mode Spectra Physics cw dye laser operating at 0.6054 μm mixed against a single axial mode Coherent Radiation argon ion laser, operating at 0.5145 μm. The dye laser was tuned to the Stokes frequency and collinearly combined with the argon ion laser beam and focussed into the gas cell. We spent considerable effort eliminating the argon ion laser plasma tube fluorescence prior to the gas cell and filtering against the 0.5145 μm light after the gas cell. The generated coherent anti-Stokes radiation at 0.4474 μm was detected with a cooled photomultiplier operating in the photon counting mode and monitored by a simple rate meter.

The line center power conversion efficiency for the parametrically generated anti-Stokes (ν_{as}) field in the low conversion regime for collinearly phase matched single axial mode pump (ν_p) and Stokes (ν_s) laser fields, interacting with an isolated Raman vibrational transition ($\nu_r = \nu_p - \nu_s$) is given by

$$\epsilon = \frac{P(\nu_{as})}{P(\nu_s)} = 2.4976\times 10^{46}(\nu_{as}^2/\nu_s^6\nu_p^2)\Delta N^2(d\sigma/d\Omega)^2 P(\nu_p)^2 l_f^2 h(r_{as}, r_s, r_p)^2 \begin{cases} 1.0266\times 10^{-2}/\Delta\nu_L^2 & \text{"homogeneous"} \\ 1.1178\times 10^{-2}/(\Delta\nu_D/\sqrt{2})^2 & \text{"inhomogeneous"} \end{cases},$$

where ν_{as}, ν_s, ν_p are in vacuum wavenumbers (cm^{-1}), the thermal equilibrium population difference $\Delta N = N(v'', J'') - N(v', J')$ (cm^{-3}), $d\sigma/d\Omega$ is the polarized component of the integrated spontaneous Raman scattering cross section for forward scattering (cm^2/sr/molecule), $P(\nu_p)$ is the incident pump field power (W), l_f is an estimated interaction length (cm) restricted by the tightness of Stokes and pump field focusing to a value less than the shorter of the gas column length or coherence length, and $h(r_{as}, r_s, r_p) = r_{as}/(\pi r_p^2 r_s/2)$ is the "near field" focusing factor for lowest order Gaussian fields where also $1/r_{as}^2 = 2/r_p^2 + 1/r_s^2$. $\Delta\nu_L$ or $\Delta\nu_D$ are the Raman full width at half maximum linewidths (Hz) for the homogeneously broadened Lorentzian limit at high pressures or the inhomogeneously broadened Doppler limit at very low pressures. When collisional narrowing effects at low gas pressures can be neglected, it can be shown that the anti-Stokes spectral density lineshape function corresponds to the spontaneous Raman pressure broadened Lorentzian lineshape at high pressures and smoothly goes into a Doppler broadened Gaussian function at very low pressures with a CARS Doppler width that is $(1/\sqrt{2})\Delta\nu_D$, where $\Delta\nu_D$ is the spontaneous Raman Doppler width for forward scattering given by $\Delta\nu_D = \nu_R[8kt\ln 2/mc^2]^{1/2}$.[8] Note that for broadband laser sources the CARS linewidth, $\Delta\nu_L$ or $\Delta\nu_D/\sqrt{2}$, must be replaced with an effective laser linewidth resulting in reduced conversion efficiency and resolution capability. With presently available "ultra high stability" narrow linewidth cw dye laser sources, pure rotational Raman transitions with corresponding Doppler linewidth of less than 1 MHz are potentially resolvable with the CARS technique.

The frequency of the $Q(\nu_1)$ Raman transition of methane is given as 2916.7 cm^{-1} (vacuum wavenumbers),[9] and we estimate $d\sigma/d\Omega = 1.5\times 10^{-30}$ cm^2/sr/molecule at

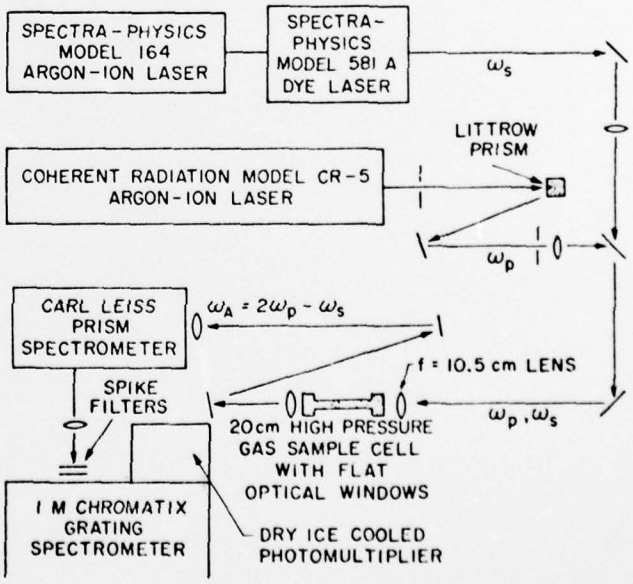

FIG. 1. Experimental layout for coherent anti-Stokes generation in methane gas at 0.4474 μm by collinear mixing of single axial mode lasers, a cw dye laser at 0.6054 μm against an argon ion laser at 0.5145 μm.

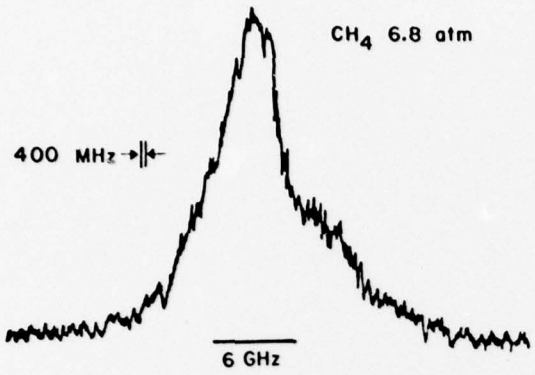

FIG. 2. CARS spectra of the $Q(v_1)$ Raman line of methane at 6.8 atm with resolution better than 400 MHz (0.013 cm^{-1}). The Raman frequency in the $v_1 = 2416.7$ cm^{-1} region is increasing from left to right.

0.5145 μm for the entire $Q(v_1)$ branch.[10] For 10 mW of cw dye laser power (6054.16 A air, 16513.0 cm^{-1} vacuum) and 640 mW of argon ion laser power (5145.23 Å air, 19429.7 cm^{-1} vacuum) incident on the 6.8 atm methane cell and focused with a 10.5 cm lens to minimum spot radii of 6 and 20 μm, respectively, we calculate a generated anti-Stokes (4473.75 A air, 22346.4 cm^{-1} vacuum) power conversion efficiency of 9.04×10^{-10} which corresponds to a peak count rate of 2.03×10^{7} at the exit window of the cell. This is based on an estimated tight focusing interaction length of 1.5 cm in the methane gas.

The measured transmittance at the anti-Stokes wavelength through the recollimating optics, prism prefilter, spike filters, and 1 m grating spectrometer was 2.94×10^{-2}. With a photocathode quantum efficiency of 18% at 0.4474 μm, we expected a count rate of 1.076×10^{5} cps at the photomultiplier. Our measured peak count rate was 1000 cps with a 50 cps background level. For this experiment our ultimate laser limited resolution of 30–50 MHz was not realized because of dye laser axial mode "hopping" instabilities common for wide range scans of over 3 GHz.

Figure 2 shows the $CH_4(v_1)$ spectra which has a measured 6 GHz linewidth. This linewidth agrees very well with a previous high resolution spectra taken by Clements and Stoicheff using a Fabey–Perot spectrometer with a 0.07 cm^{-1} resolution.[9]

Considerable improvement in the signal level can be obtained by improved spectral filtering efficiency (~10×), phase sensitive detection in sychronism with a chopped dye laser (~10×) and by resonating the single mode pump laser field in an external cavity around the gas cell (~100×). With these experimental improvements the cw CARS signal level should increase by 10^4 to approximately 10^9 cps. cw CARS is a spectroscopic technique that for the first time offers the capability of fully resolving the Raman spectra of molecular gases.

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APPENDIX III

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Bulletin Subject Heading in which Paper should be placed
Raman Spectroscopy

B.C.1. Collisionally Narrowed Lineshape of Raman Q Branch Lines of H_2 and D_2. M.A. HENESIAN, R.L. BYER*, Stanford University and L. KULEVSKII, Lebedev Physical Institute--
The collisionally narrowed lineshape of the Raman Q(1) 4155.21 cm^{-1} line of H_2 and the Q(2) 2987.18 cm^{-1} line of D_2 has been investigated at room temperature from the pressure broadened regime, through the collision narrowed minimum, to the Doppler broadened limit at low pressure utilizing the coherent anti-Stokes Raman (CARS) four wave mixing technique. The resolution, limited by the relative stability of the single axial mode dye laser and argon-ion laser, was better than 40 MHz. For H_2 we measured a minimum collision narrowed linewidth (FWHM) of 290 MHz at 3.0 atm and for D_2 a minimum linewidth of 260 MHz occuring at 1.3 atm. Below 30 atm we estimate pressure broadening coefficients of 1.26×10^{-3} cm^{-1}/atm and 3.50×10^{-3} cm^{-1} atm and self-diffusion coefficients of * ~~2.42~~ cm^2/S and ~~1.41~~ $cm^2/5$ for H_2 and D_2 respectively. This is the first experiment performed that demonstrates the ultra-high resolution potential for cw CARS in the field of gas phase Raman spectroscopy.
*Work supported by Sloan Fellowship 1974-1976.

* CORRECTION 12/20/76 M.H.
H_2 : 1.56 $CM^2ATM/5$
D_2 : 1.62 $CM^2ATM/5$
AT 20 °C.
THE VALUE OF THE SELF-DIFFUSION COEFFICIENT FOR D_2 IS ANOMALOUSLY LARGE. BASED ON H_2 ONE WOULD ESTIMATE 1.10 $CM^2ATM/5$ FOR D_2.

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